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ATTENUATION MEASUREMENTS OF ULTRASONIC
WAVES IN MANGANESE FLUORIDE IN THE
REGION OF THE NEEL TEMPERATURE

CARL S. MORSE
and
PHILIP OLIVER

ATTENUATION MEASUREMENTS OF ULTRASONIC WAVES IN MANGANESE
FLUORIDE IN THE REGION OF THE NÉEL TEMPERATURE

* * * * *

Carl S. Morse

and

Philip Oliver, Jr.

ATTENUATION MEASUREMENTS OF ULTRASONIC WAVES IN MANGANESE
FLUORIDE IN THE REGION OF THE NÉEL TEMPERATURE

by

Carl S. Morse

Lieutenant, United States Navy

and

Philip Oliver, Jr.

Lieutenant Commander, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

1 9 6 5

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This work is accepted as fulfilling
the thesis requirements for the degree of

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PHYSICS

from the

United States Naval Postgraduate School

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ABSTRACT

Measurements of the attenuation of ultrasonic waves in MnF_2 were made in region of the Néel temperature (67.336°K). Longitudinal waves were propagated at 25.7 Mc and 35.8 Mc along the c-axis, and at 26.2 Mc and 37.2 Mc along the $[110]$ direction. The attenuation peaked at 67.204°K at 35.8 Mc and at 67.206°K at 25.7 Mc for propagation along the c-axis, and at 67.080°K at 37.2 Mc and at 67.128°K at 26.2 Mc in the $[110]$ direction. Shear waves were propagated at 12.5 Mc and 33.6 Mc along the c-axis, and parallel to the a-axis. No attenuation peak was observed for the shear wave. In both longitudinal and shear waves the attenuation increased with increasing frequency.

Elastic constants determined were:

C_{33}	$17.99 \times 10^{11} \text{ dynes/cm}^2$
$\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{66}$	$17.47 \times 10^{11} \text{ dynes/cm}^2$
C_{44}	$9.469 \times 10^{11} \text{ dynes/cm}^2$

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INTRODUCTION

Manganese fluoride (MnF_2) has been investigated extensively because of anomalies appearing near the Néel temperature (T_n) in such properties as magnetic susceptibility, specific heat, thermal expansion, neutron scattering, nuclear magnetic resonance frequency and mechanical properties. One of the more recent of these investigations by J. R. Neighbours, R. W. Oliver and C. H. Stilwell in 1963 dealt with the mechanical properties in the [110] direction. (1) They found that for frequencies between 8 to 65 Mc a peak in attenuation of longitudinal waves through the crystal, occurred at 67.35 ± 0.02 °K, which is very close to the reported Néel temperature of 67.336 °K. (2) The attenuation was also found to increase with increase in frequency. For shear waves the attenuation also increases with frequency but no peak was obtained as with longitudinal waves. These findings were reviewed in detail by M. Papoular, Faculté de Sciences, University of Paris in 1964. (3) It is his considered opinion that investigations in the [001] direction will show a frequency dependent attenuation peak somewhere below the Néel temperature. Since no experimentation has been done to verify his theory, the present work of observing the attenuation of longitudinal and shear waves in MnF_2 along the c-axis was undertaken.

EXPERIMENTAL PROCEDURE

A single MnF_2 crystal, approximately $2 \times 2 \times 3$ cm., was obtained for experimental use. Initial Laue back reflection X-ray patterns showed the crystal to be randomly oriented. From successive X-ray patterns the direction of the c-axis was determined. Knowing the direction of the c-axis two faces normal to it were ground.

The rough grinding of these faces was accomplished by power grinding with a water cooled jeweler's abrasive disc. Preliminary rough grinding with scrap chips of MnF_2 showed that dry grinding would cause cracking of the crystal where water cooling would not. A holder was fabricated from aluminum stock approximately six inches long with a cup configuration at one end. The holder was attached to the cross feed carriage of the power grinder. The cup accommodated the properly oriented crystal which was held in place by sealing wax. The entire holder assembly was immersed in an ice bath prior to grinding to insure as rigid a bond as possible. With this method the two coplanar surfaces were ground. Laue X-ray patterns were again taken at this point to assure c-axis orientation.

The two faces were smooth polished to a room temperature crystal thickness of $1.2852 \pm .0015$ cm, using dry 1/0, 2/0, 3/0 emery cloth on a polishing glass plate as a plane surface. A machined steel annular holder was used to assure that the finished faces would be parallel. The crystal inserted in the holder and held in place with sealing wax. The use of the machined holder assured the polished crystal faces would be parallel with as close a tolerance as can be expected with hand polishing procedures.

It was found that the best crystal holder configuration, with certain modifications, was the one used by Stilwell and Oliver in their thesis

work. (4) All resistance coils and wiring used in the previous work were removed. A single #32 copper wire r-f lead was installed, the holder providing the electrical return. A copper resistor was installed for temperature determination. One hundred feet of #42 copper wire was wound non-inductively on a brass spool and attached to the base of the holder. The wire leads to the resistor were #32 copper for minimum resistance relative to the wound resistor. In the region of liquid nitrogen (N_2) temperatures the coil resistance can be determined to an accuracy of ± 0.001 ohms using a Wheatstone bridge and galvanometer. The external wiring used for r-f and the resistance leads was Belden 8216 RG-174/U. The holder was placed in a vacuum system and tested to assure that there were no leaks. Figure 1 shows the final configuration of the crystal holder used.

The crystal was placed in the holder in the same manner as was done by Stilwell and Oliver. However it was found that the bonding material (Dow-Corning 710) used by them was not satisfactory. Several materials were tested and it was found that #792191 Nonaq Stopcock Grease (Fischer Scientific Co.) provided an excellent bond in conjunction with liquid nitrogen immersion. Because the bonding material has a tendency to absorb water, care was taken to assure fresh bonds with every run.

The transducer used to provide longitudinal waves was 3/8 inch, 10 Mc, X-cut piezoelectric quartz. The same bond was used to secure the transducer to a 0.001 cm aluminum coated mylar film. For shear waves a Y-cut, 3/8 inch, 10 Mc piezoelectric quartz transducer was used.

A schematic diagram of the electronic equipment used in this work is shown in Figure 2. Short radio frequency waves were generated by an Arenberg Pulsed Oscillator with a pulse length of two microseconds and with a spacing of 1000 pulses per second. This allowed ample time for

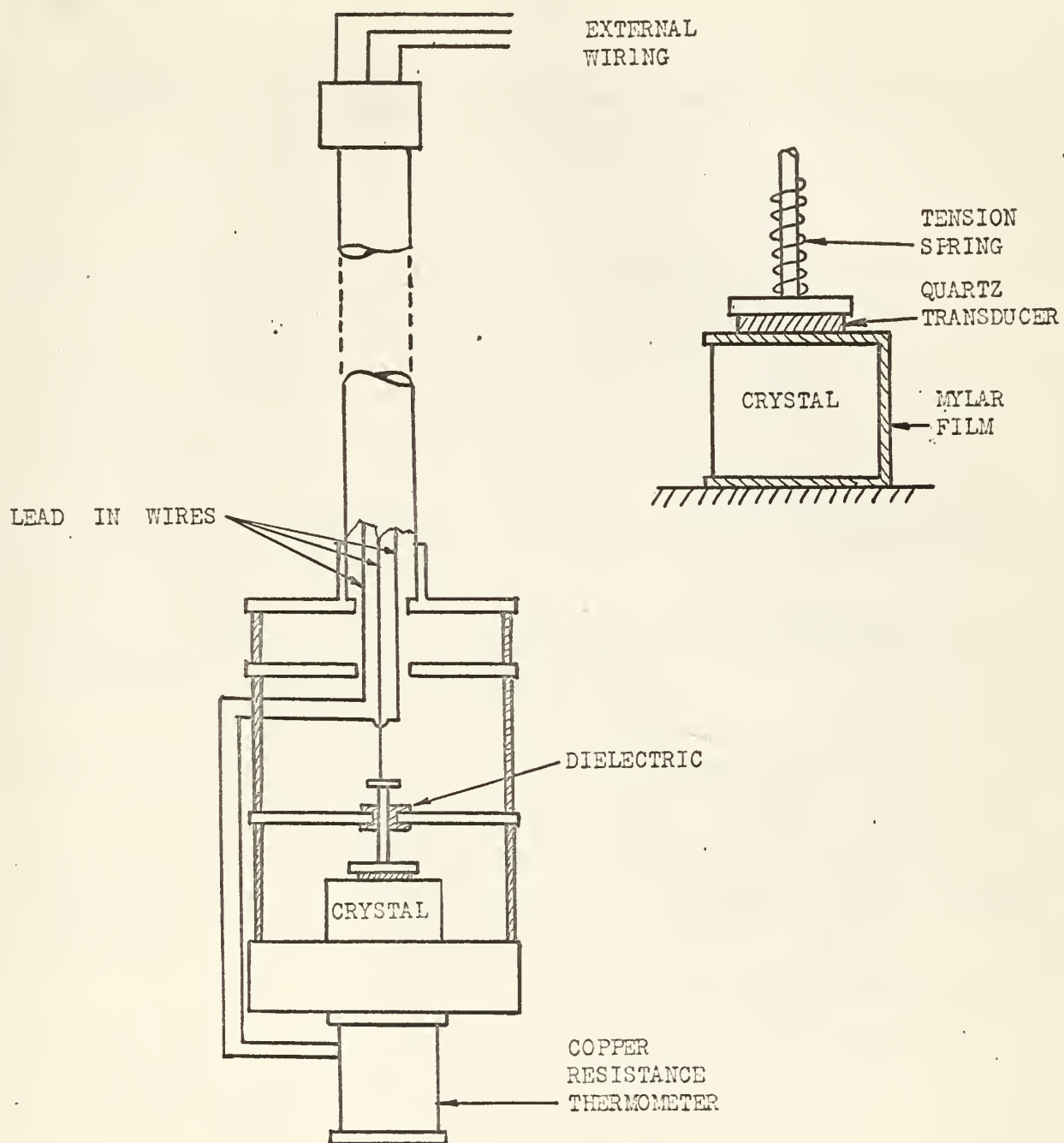


FIGURE 1
CRYSTAL HOLDER

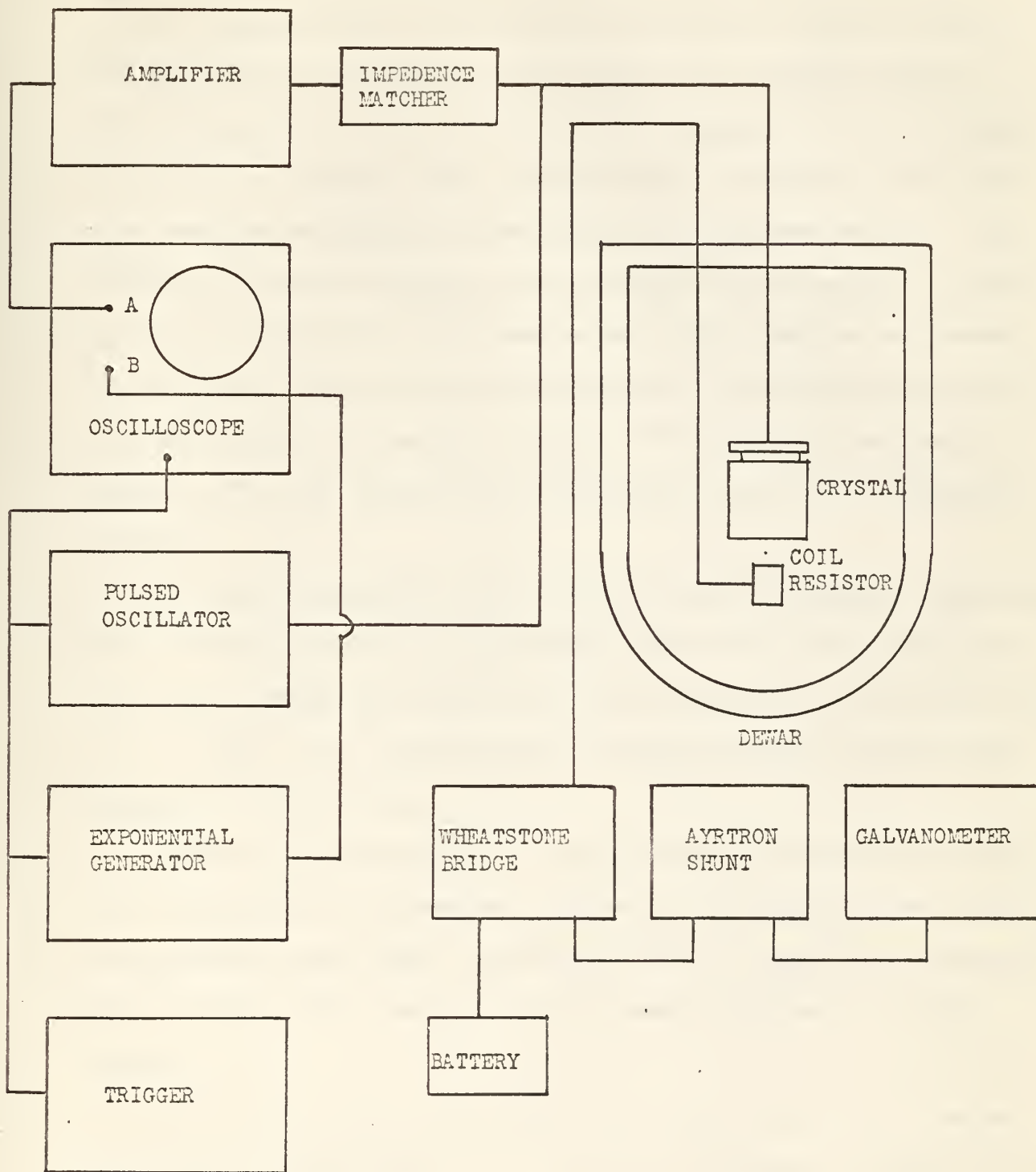


FIGURE 2
ELECTRONIC EQUIPMENT

measurement of the returning echo. Radio frequency waves produced sound waves in the quartz transducer; these waves were transferred to the crystal through the bond. The sound wave travelled through the crystal and was reflected from the far surface back to the transducer where it was reconverted to r-f and the echo pattern displayed on the oscilloscope in proper time relation to the original pulse. An exponential wave was also generated and displayed simultaneously with the echo pattern. The exponential wave when matched to the envelope of the echos gave an indication of the attenuation of the sound waves in the crystal at any instant. The exponential wave generator was calibrated to provide the time constant for any setting on the variable resistor of the generator, as shown by Figure 3. The time constants were subsequently converted to attenuation in db/cm.

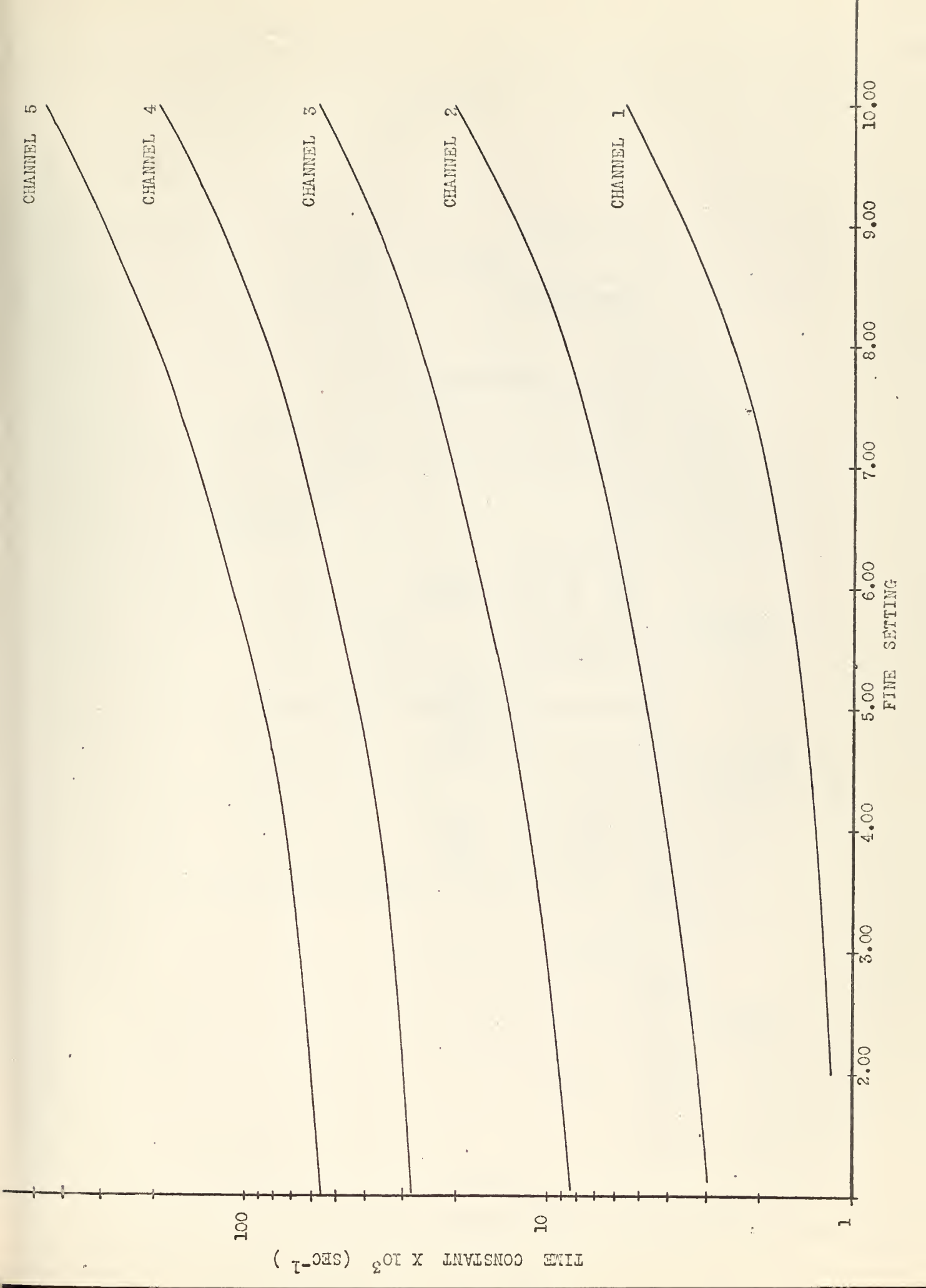
For those echo patterns that could not be matched with the exponential wave, it was necessary to use photographs taken on the oscilloscope displays, and attenuations computed using the single echo picture method used by J. P. Goncz. (7) His method gave consistent results with the method exponential wave matching.

Because (a) vapor pressure of liquid nitrogen can be directly converted to temperature by an empirical relation (5), (b) liquid N_2 falls within the temperature range under consideration, and (c) liquid N_2 is relatively safe to handle, this cryogenic fluid was used in preference to liquid oxygen.

A vacuum system was used to pump on the liquid N_2 to give a temperature range from approximately 70° K to 65° K, a schematic of which is shown in Figure 4. A glass dewar in the system was used to contain the immersed

Figure 3

Time constant versus variable resistor setting of the exponential wave generator



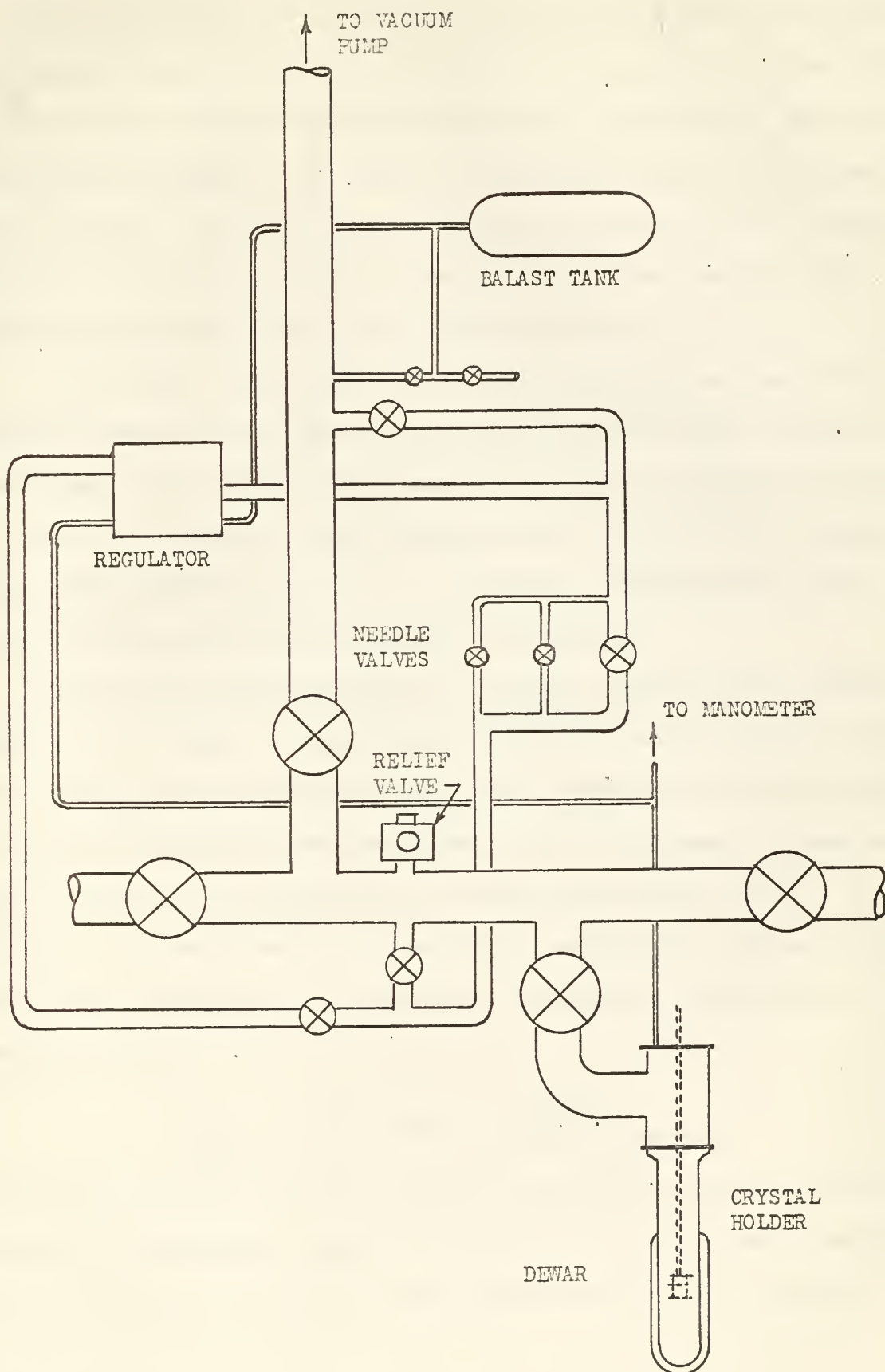


FIGURE 4
VACUUM SYSTEM

crystal in liquid N_2 . To assure vapor pressure measurements, continuous boiling was effected by the use of porcelain boiling stones. Before filling with liquid nitrogen the vacuum system was flushed with N_2 gas to displace the air present in the system. The cryogenic fluid was then introduced directly. Since the presence of any foreign gas in the system with N_2 will give a false temperature reading for N_2 it was important that these precautions were taken when filling the dewar.

Transit time of the sound wave through the crystal was measured from the oscilloscope display by measuring successive echo pulses. Knowing the path length of the crystal the velocity of the wave is readily obtainable.

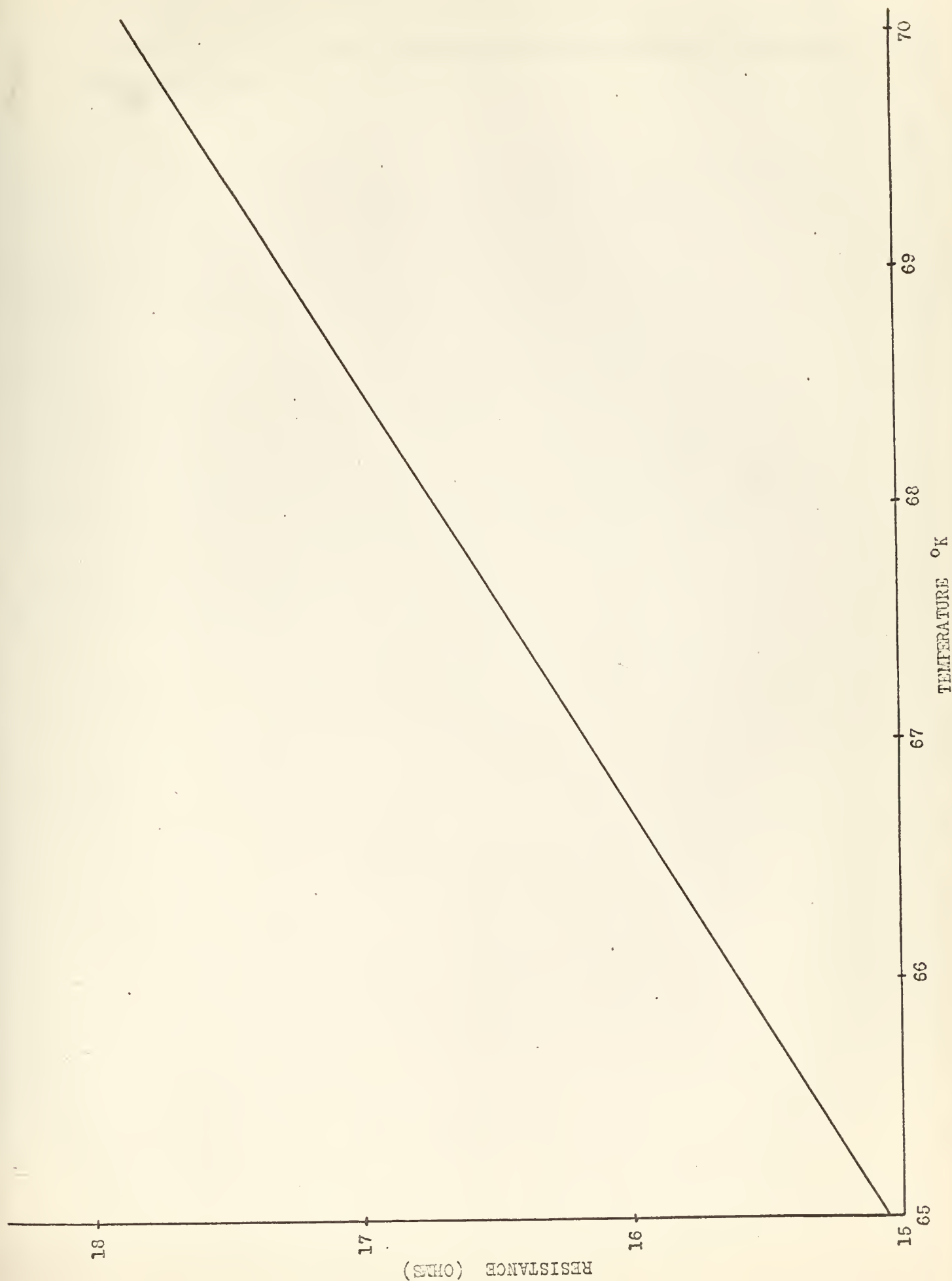
The total change in length of MnF_2 between 0° and $273.2^\circ K$ is approximately 0.3% along the c-axis. (6) Accordingly, expansion along the c-axis for the purpose of this experiment was ignored.

Vapor pressure was measured with a mercury manometer which could be read to ± 0.01 mmHg. A vacuum gauge was used as a back-up pressure reading. The resistance thermometer was used to assure the following conditions; (a) that equilibrium was reached after an incremental change in vapor pressure by the balancing of the Wheatstone bridge, and (b) to serve as the primary back-up for temperature measurement. The corresponding pressure readings at equilibrium were converted to temperature by the empirical relation: (5)

$$\text{Log}_{10} P(\text{mm.}) = 6.49594 - \frac{255.821}{T(^{\circ}K) - 6.600}$$

The equilibrium resistances read from the Wheatstone bridge were plotted against the corresponding equilibrium temperatures. This gave a continuous calibration of resistance versus temperature as shown in Figure 5.

Figure 5
Resistance versus temperature



The resistance versus temperature plot was consistent for all runs made. A correction for the head of liquid N_2 above the crystal was included in all computations.

EXPERIMENTAL RESULTS

Investigation of attenuation along the c-axis for both longitudinal and shear sound waves was conducted. In addition longitudinal waves in the [110] direction using the Stillwell and Oliver MnF_2 crystal were investigated to see if their results could be reproduced using the methods of this experiment. The following results were found:

The temperature range for all the runs was from 65° to 70° K, this being the range of interest around the Néel temperature. For longitudinal waves propagated along the c-axis the frequencies used were 25.7 Mc and 35.8 Mc. For shear waves propagated along the c-axis and parallel to the a-axis the frequencies used were 12.5 Mc and 33.6 Mc. Frequencies of 26.2 Mc and 37.2 Mc were used for longitudinal waves along the [110] direction. The selection of these particular frequencies were made because they displayed optimum echo patterns.

For longitudinal waves in both directions of propagation the sound velocity was constant with frequency and temperature over the ranges considered. The velocity along the c-axis was 6.80×10^5 cm/sec, and 6.70×10^5 cm/sec along the [110] direction.

For shear waves the sound velocity was also constant with temperature and frequency, and was determined to be 1.56×10^5 cm/sec.

The attenuation of longitudinal waves was both frequency and temperature dependent over the ranges considered in that attenuation increased with increase in frequency. The attenuation peaked at 67.204° K at 35.8 Mc and at 67.206° K at 25.7 Mc for propagation along the c-axis, and at 67.080° K at 37.2 Mc and at 67.128° K at 26.2 Mc in the [110] direction. Figures 6 and 7 are plots of attenuation as a function of temperature for the frequencies used, and show these peaks.

Figure 6

Attenuation versus temperature for longitudinal waves propagated along the c-axis in MnF_2

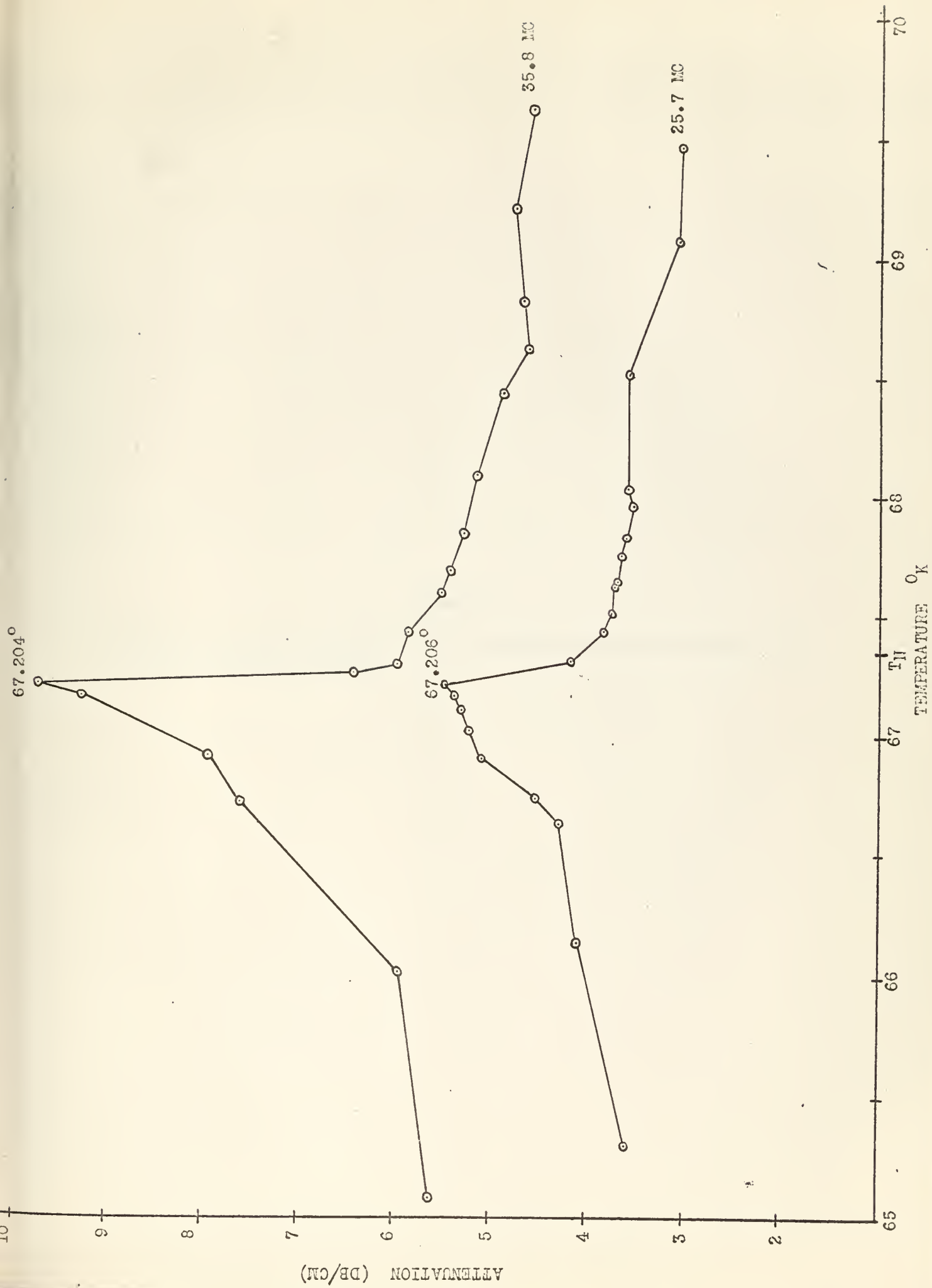


Figure 7

Attenuation versus temperature for longitudinal waves propagated along the [110] direction in MnF_2

5.4

ATTENUATION (DB/CM)

4.8

4.2

3.6

3.0

67.080°

67.128°

26.2 MC

37.2 MC

TEMPERATURE °K

68

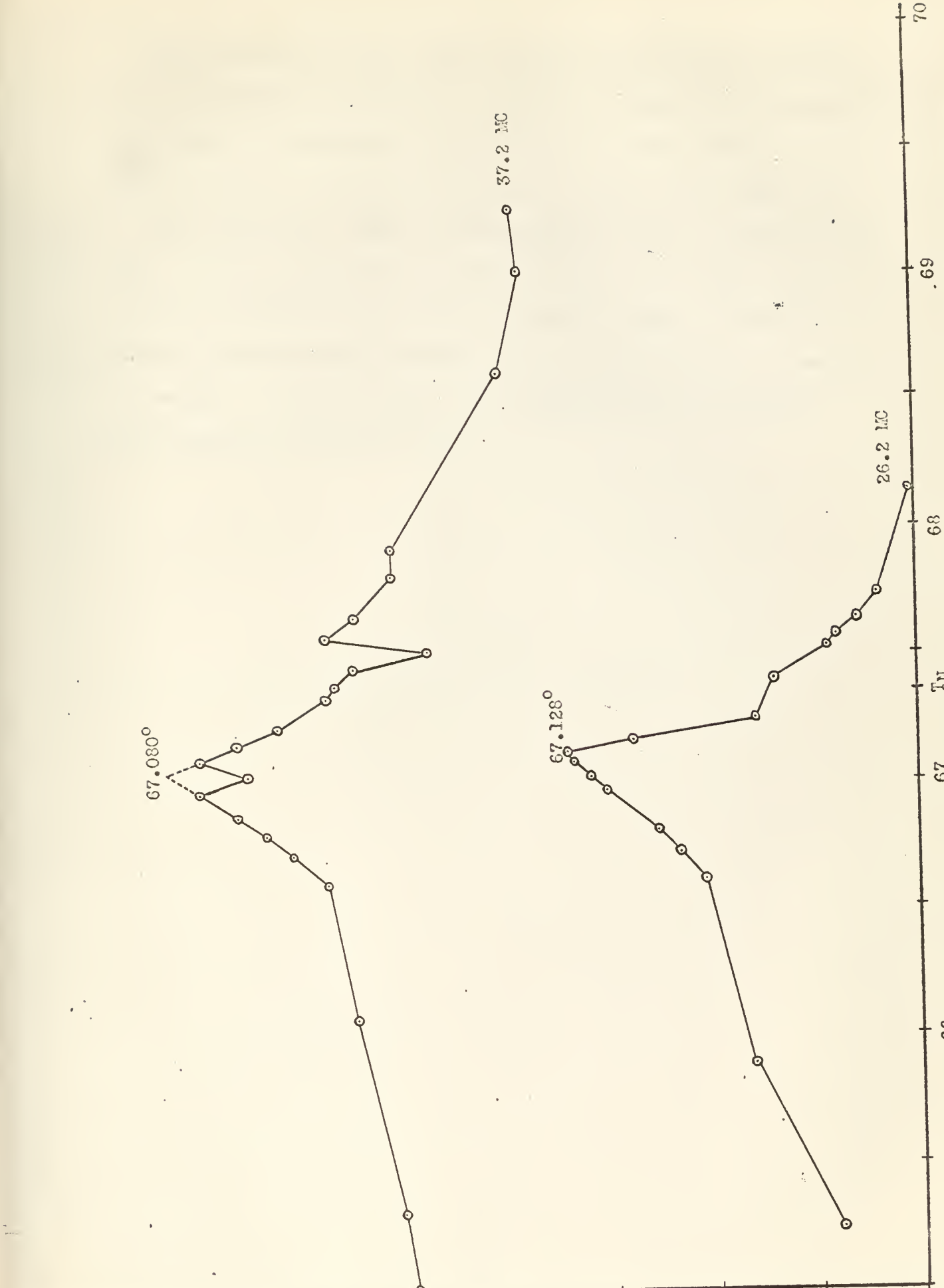
67

66.

65

.69

70

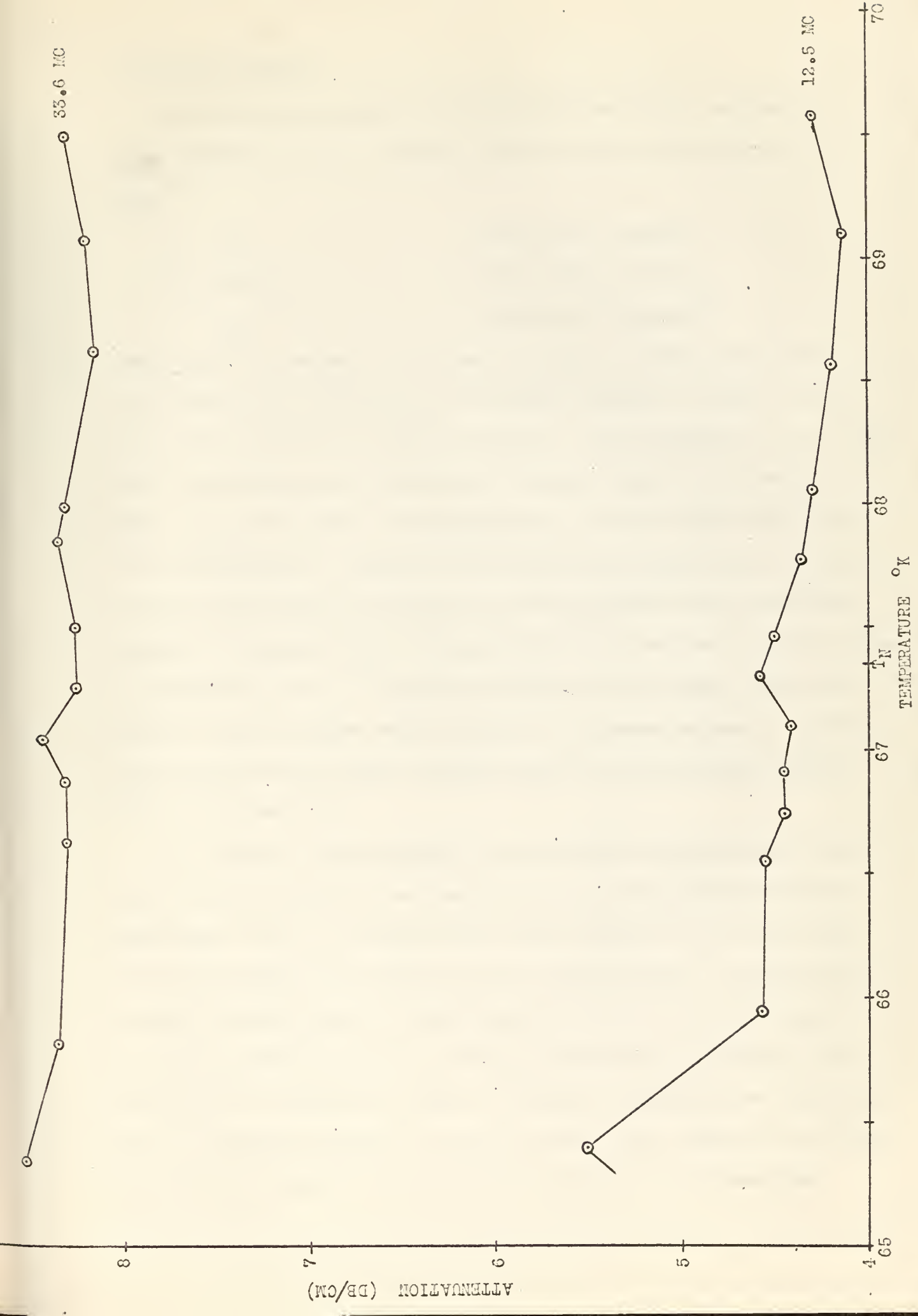


The attenuation of shear waves was found to be frequency dependent in that attenuation increased with increase in frequency, but inconclusive with respect to temperature as can be seen by the fluctuations of the plots in Figure 8. No definite peaking was detected using shear waves.

Six longitudinal c-axis runs were performed prior to those reported herein. However, they are not included as part of this report because of imperfect thermometry at the time the runs were made. It should be noted that the same general configuration of attenuation versus temperature existed and that all peaks occurred somewhere below the reported Néel temperature and above 67.00° K.

Figure 8

Attenuation versus temperature for shear waves propagated along the c-axis and parallel to the a-axis in MnF_2



Discussion of Results

Using the approximation for determination of elastic constants of single crystals (8), the following elastic constants are calculated for MnF_2 :

C_{33}	$17.99 \times 10^{11} \text{ dynes/cm}^2$
$\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{66}$	$17.47 \times 10^{11} \text{ dynes/cm}^2$
C_{44}	$9.469 \times 10^{11} \text{ dynes/cm}^2$

Comparing these constants with those calculated by Oliver and Stilwell (4) it is noted that $\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{66}$ is in general agreement. However, the results of C_{44} differ by a factor of about 3. This discrepancy is very large and is the result of the difference in measured values of the transit time, which could be the result of misreading the time scale and/or echo pulses of the oscilloscope. However if polarizations for shear waves as reported by Oliver and Stilwell are reversed, then the velocity for the shear wave propagation along the c-axis and parallel to the a-axis is $1.62 \times 10^5 \text{ cm/sec}$ as compared to $1.56 \times 10^5 \text{ cm/sec}$ reported in this experiment. The corresponding elastic constant would therefore be in general agreement. Further investigation of C_{44} should be made to reconcile the difference between the two reported values.

The values of peak attenuation for longitudinal waves measured along the c-axis are found to be at temperatures lower than the reported Néel temperature. Also, in comparing the results obtained in this experiment with that of Oliver and Stilwell for the [110] direction, the temperature at which the peaks occur are lower than what Oliver and Stilwell report. In this experiment all data is taken at equilibrium as indicated by the balancing of the Wheatstone bridge. A possible explanation for the difference in reported temperature at which the peaks occur, would be the different methods of temperature determination employed. In this experiment

the temperature is determined from nitrogen vapor pressure; whereas, Oliver and Stilwell employed a platinum resistor calibrated against vapor pressure of liquid oxygen to determine temperature. In this experiment it was necessary to use more than one source of liquid nitrogen. Therefore, if there were any impurities and if they varied from source to source, results obtained for this experiment could be expected to vary.

According to theory (9), in the range of frequencies used in this experiment, the attenuation is directly proportional to the frequency squared and maximum for $T=T_n$, for a first order transition. For a second order transition in the same frequency range, attenuation is directly proportional to the frequency and shifts to lower temperatures at higher frequencies.

Analyzing the data for longitudinal waves along $[110]$, the attenuation varies approximately directly as the frequency and shifts to a lower temperature at the higher frequency. Looking at the data reported by Oliver and Stilwell for the same direction, the attenuation is approximately proportional to the frequency. The implication here is that for longitudinal waves along $[110]$, one can expect to find second order transition.

However, the data for longitudinal waves along the c-axis shows that the attenuation varies approximately as the frequency squared and the peak temperatures are approximately constant.

Two possible conclusions which can be inferred from the above are:

1. That both first and second order transitions occur in MnF_2 and are dependent upon direction.
2. That the number of frequencies used is insufficient to draw any conclusions as to the transition order.

With respect to the attenuation of shear waves, the results obtained are similar to those obtained by Oliver and Stilwell in that the shear waves show a frequency dependence but do not show any conclusive temperature dependence. According to Papoular (3), a possible explanation for not observing an attenuation peak for these shear waves is the smallness of the spin phonon coupling constant as compared to this constant relative to longitudinal phonons. With respect to obtaining an echo pattern for longitudinal waves, it was found that establishing echo patterns for shear waves presented more of a problem.

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APPENDIX I

CALCULATIONS

1. Calibration of Exponential Wave Generator Using Wave Displayed on Oscilloscope. ($\lambda \text{ sec}^{-1}$)

$$V = V_0 e^{-\lambda t}$$

where V = voltage at any time t
(vertical axis)

$$\text{when } \frac{V}{V_0} = \frac{1}{2}$$

V_0 = voltage at time $t = 0$
= time constant, sec^{-1}

t = time in sec (horizontal axis)

$$\text{then } = \frac{\ln 2}{t_{\frac{1}{2}}}$$

Time constant was determined for various settings of the exponential wave generator and plotted in Figure 3.

2. Sound Wave Velocity ($v \text{ cm/sec}$)

$$v = \frac{2d}{t}$$

where d = thickness of crystal in cm
 t = transit time in sec

a) Propagation along c-axis with longitudinal wave

$$v = \frac{2 \times 1.2852}{3.78 \times 10^{-6}} = 6.80 \times 10^5 \text{ cm/sec}$$

b) Propagation in the $[110]$ direction with longitudinal wave

$$v = \frac{2 \times 1.386}{4.14 \times 10^{-6}} = 6.70 \times 10^5 \text{ cm/sec}$$

c) Propagation along the c-axis with shear wave parallel to a-axis

$$v = \frac{2 \times 1.2852}{16.5 \times 10^{-6}} = 1.56 \times 10^5 \text{ cm/sec}$$

3. Attenuation ($\propto \text{db/cm}$)

$$\alpha = \frac{\lambda k}{v}$$

where λ = time constant in sec^{-1}
 v = velocity in cm/sec
 k = 20 times the conversion
from \log_{10} to \ln based on
relation,

$$\alpha = \frac{\lambda \times 8.6858}{v}$$

$$\text{db} = 20 \log_{10} \frac{V}{V_{\text{ref}}} = (.43429) 20 \ln \frac{V}{V_{\text{ref}}}$$

4. Temperature (T K)

$$T = 6.600 + \frac{255.821}{6.49594 - \log_{10} P}$$

where P is the corrected manometer reading in mmHg. The correction was made for liquid N₂ head as follows

$$\frac{1\text{mm N}_2}{1\text{mm Hg}} = \frac{\text{density liquid N}_2 @ 77^\circ \text{K}}{\text{density Hg @ 293}^\circ \text{K}} = \frac{0.808}{13.546} = 0.0596$$

5. Elastic Constants (dynes/cm²)

Density of MnF₂ as listed in ASTM file is 3.891 gm/cm³.

a) Propagation along c-axis with longitudinal wave

$$\begin{aligned} C_{33} &= \rho v_1^2 \\ &= 3.891 \text{ gm/cm}^3 \times (6.80 \times 10^5 \text{ cm/sec})^2 \\ &= 17.99 \times 10^{11} \text{ dyne/cm}^2 \end{aligned}$$

b) Propagation in the [110] direction with longitudinal wave

$$\begin{aligned} \frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{66} &= \rho v_1^2 \\ &= 3.891 \text{ gm/cm}^3 (6.70 \times 10^5 \text{ cm/sec})^2 \\ &= 17.47 \times 10^{11} \text{ dyne/cm}^2 \end{aligned}$$

c) Propagation along the c-axis with shear waves parallel to

a-axis

$$\begin{aligned} C_{44} &= \rho v_t^2 \\ &= (3.891 \text{ gm/cm}^3) \times (1.56 \times 10^5 \text{ cm/sec})^2 \\ &= 9.469 \times 10^{11} \text{ dyne/cm}^2 \end{aligned}$$

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